Soil Acidity in Loblolly Pine Stands with Interval Burning[1]

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ABSTRACT

Prescribed burning of loblolly pine (*Pinus taeda* L.) stands every 2 yr for 24 yr increased soil pH by 0.3 to 0.9 units. Measurements of total acidity (titratable to pH 8.2) in the forest floor showed about a 14 to 21 kmol H^+ ha^{-1} decrease in burned plots. Burning increased the acid neutralizing capacity per gram of forest floor material, but the reduction in forest floor biomass largely offset the difference. Titration curves indicated that the burned forest floor would require only about 0.6 kmol H^+ ha^{-1} to lower its pH to the level of the control plots. Total acidity in the 0 to 10 cm mineral soil was more variable; one burned plot showed no decrease relative to controls, but a more intensely burned plot decreased by about 95 kmol H^+ ha^{-1}. Despite this large reduction in total acidity, titration curves indicatd that only 25 kmol H^+ ha^{-1} would lower the pH to the control level. This increase in acid neutralizing capacity is about 50 times the current annual H^+ input in rain. However, other major components of the ecosystem's H^+ budget would need to be quantified to assess the importance of fire in relation to acid deposition impacts.

Additional Index Words: acid deposition, pH, prescribed burning, titration curves.

ABOUT 1 MILLION HA OF PINE FORESTS are prescribed burned each year in the southeastern USA (Richter et al., 1982). Soil pH in burned soils is often 0.3 to 1.0 unit higher than in unburned soils, but some low-intensity fires do not change pH (Wells et al., 1979; McKee, 1982). Reductions in soil acidity are often attributed to the release of so-called base cations (Raison, 1979; Wells et al., 1979; Chandler et al. 1983). However, these cations are not bases in a chemical sense, and the decrease in acidity derives from consumption of H^+ to produce H_2O and CO_2 during combustion of dissociated organic acids and of organic molecules containing cation nutrients. The consumption of H^+ generates OH^-, which forms hydroxides and then carbonates with cations.

The change in soil pH following fire depends on both the quantity of H^+ consumed and the equilibrium between H^+ free in soil solution (measured as pH) and the large pools of H^+ measured as exchangeable and total acidities (see Adams, 1984). The exchangeable pool consists of H^+ and Al on cation exchange sites (plus the H^+ free in soil solution unless this component is subtracted). Hydrated Al suplies H^+ to the soil solution as pH of the solution increases. The total pool (typically titrated to pH 8.2) consists of the exchangeable pool plus the H^+ that can be removed by titration with OH^- from organic acids and Al not included in the exchangeable pool. The free acidity of a soil typically comprises a very small fraction of the total soil acidity, and pH is regulated by a

dynamic interaction with the less reactive pools of H^+. Many studies have measured the change in soil pH following fire, but the rest of the acidity picture remains largely unexamined. In this study, we measured the net changes in soil acidity resulting from prescribed fires every 2 yr for 24 yr in a loblolly pine plantation.

SITE DESCRIPTION AND METHODS

The research installation was established and maintained by USDA Forest Service researchers from the Forest Fire Research Project headquartered in Macon, GA. Located in the Francis Marion National Forest in South Carolina, the research plots were on a Lynchburg series soil (fine loamy, siliceous, thermic Aeric Paleaquult). The forest was a 56-yr-old stand with basal area of about 23 m^2 ha^{-1}, dominated by loblolly pine (*Pinus taeda* L.), with longleaf pine (*P. palustris* Mill.), and pond pine (*P. serotina* Michx.), accounting for about a third of the basal area. Replicatcd 0.8 ha plots have been left unburned, or burned at intervals of 1, 2, 3, or 4-yr since the winter of 1959 to 1960.

In Feb. 1985, we sampled 2 plots of the 2-yr-interval (last burned in Feb. 1984) and 2 control plots. At the time of the last fire (data supplied by D. Wade, Feb. 25, 1985, personal communication), Burn A plot had a basal area of about 20 m^2 ha^{-1}, and Burn B had about 33 m^2 ha^{-1}. The difference in basal area was reflected in the pre-burn weights of the forest floors: 13 Mg ha^{-1} for Burn A, and 24 Mg ha^{-1} for Burn B. The fire consumed more than twice as much material in Burn B (17 Mg ha^{-1}) than in Burn A (6.5 Mg ha^{-1}). The lower consumption in Burn A may relate to lower fuel loading, but some may also be due to an unplanned drop of fire retardant on part of the plot about 30 min after ignition.

Twelve forest floor samples were collected from a 0.10 m^2 frame at 6-m intervals along a transect through the middle of each plot. Six mineral soil samples (0–10 cm depth) were taken with a 10-cm diam core at 12-m intervals along the same transects. Forest floor samples were sieved in the laboratory; the >4-mm fraction (Oi) was air-dried and ground, and the <4-mm Oi fraction (Oe+Oa) was stored at 4°C until analyzed. Mineral soil samples were also stored cold until analyzed (<4 weeks).

Cation exchange capacity (CEC) was determined by saturating exchange sites with 1 M KCl, followed by alcohol rinses and replacement with 1 M NaCl (Method 8.3, Lavkulich, 1976). Soil pH measurements were made in a paste of soil and deionized water and also in 0.01 M CaCl$_2$. Titration curves were obtained by adding incremental amounts of dilute HCl or NaOH, with 24-h equilibration time before pH measurement. This period was chosen because pH remained constant from 12 through 36 h after addition of acid or base. Exchangeable acidity was determined by titration of a filtered, 1 M KCl extract to a phenolphthalein endpoint, and the contribution from Al was determined by adding KF (Method 9-4.2, Thomas, 1983). This method probably overestimates Al concentrations by 10 to 50% because both Al(OH)$_3$ and Al(OH)$_4^-$ would be present at pH 8.3 (Logan et al. 1985). Total acidity was determined by the Ba-Cl-tri-ethanolamine method, with titration to a bromocresol endpoint (Method 9-4.1, Thomas, 1983). Forest floor weights and mineral soil bulk densities were used to convert values from a weight basis to an areal basis.

Because the intensity of the most recent fire clearly differed between the burned plots, statistical analyses were per-

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formed independently on each plot rather than by treatment groups. Analysis of variance and Tukey's Honestly Significant Difference tests were calculated with SYSTAT Version 2.1 (Wilkinson, 1985) for MS-DOS microcomputers, with a significance level of $p \leq 0.05$.

RESULTS AND DISCUSSION

In February, 1985, the forest floor weights of the burned plots differed significantly from each other and from the two control plots (Table 1). The soils in all plots were extremely acidic: only the more intensely burned plot (Burn B) showed a mineral soil pH (water) above 4.0 (Table 2). Exchangeable acidity comprised about 20% of the CEC, except on the more-intensely burned plot where it comprised only 12% (Table 3). About 80% of the exchangeable acidity was derived from exchangeable Al. The burning regime reduced CEC, exchangeable acidity, and total acidity of the forest floor in both plots (Table 3). The proportional reduction in acidity was greater for the exchangeable pool than for the total pool. The reduction in total acidity of the forest floor averaged about 14 to 21 kmol H^+ ha^{-1}. In the mineral soil, both CEC and exchangeable acidity were lower on burned plots, but titratable acidity showed no significant differences among plots. However, the combined decrease of about 120 kmol H^+ ha^{-1} in the mineral soil plus forest floor in the

more intensely burned plot was significantly lower than the controls.

Two approaches can be used to examine changes in pH as a function of changes in acid pools. The pattern of pH and total acidity among samples from all plots can be calculated (correlation coefficients in Table 4) and graphed (Fig. 1). Based on linear regressions, a decrease of about 15 kmol H^+ ha^{-1} of total acidity in the Oi horizon would provide a 0.5 unit increase in pH (water). For the Oe + Oa, the relationship between total acidity and pH appeared curvilinear. Below about 20 kmol H^+ ha^{-1}, a 0.5 unit increase in pH would result from a 2.5 kmol H^+ ha^{-1} decrease in total acidity. Above 20 kmol H^+ ha^{-1}, the pH of the Oe + Oa appeared well buffered at 3.5. In the 0 to 10 cm

Table 1. Mean ash-free forest floor weights of control and burned plots in Feb. 1985.

Horizon	Plot			
	Control A	Control B	Burn A	Burn B
	Mg ha⁻¹			
Oi	14.7 (1.2)c†	12.5 (1.3)c	8.6 (0.9)b	6.3 (0.5)a
Oe + Oa	14.9 (1.7)c	13.2 (1.5)c	7.7 (1.0)b	3.2 (0.7)a
Sum	29.6 (2.3)c	25.7 (2.7)c	16.3 (1.9)b	9.5 (0.9)a

† Standard errors in parentheses, $n = 12$ per stand. Common letters among means denote no significant difference at $p \leq 0.05$.

Table 2. Mean pH and free acidity.

Parameter	Plot							
	Control A		Control B		Burn A		Burn B	
	pH	mol H⁺/ha	pH	mol H⁺/ha	pH	mol H⁺/ha	pH	mol H⁺/ha
In water								
Oi	3.73 (0.04)c†	8.6 (1.4)b	3.77 (0.03)c	6.5 (1.1b)	3.92 (0.02)b	3.2 (0.5)a	4.03 (0.02)a	1.8 (0.3)a
Oe + Oa	3.48 (0.03)c	14.9 (2.9)c	3.28 (0.17)c	14.9 (3.4)c	3.62 (0.04)b	5.5 (1.0)a	4.23 (0.16)a	0.8 (0.3)a
Mineral soil	3.70 (0.08)b	311 (12)b	3.78 (0.03)b	259 (5)b	3.77 (0.07)b	268 (11)b	4.12 (0.10)a	120 (16)a
In 0.012 M CaCl₂								
Oi	3.57 (0.04)d	12.4 (2.0)d	3.68 (0.03)c	8.0 (1.4)c	3.87 (0.04)b	3.2 (0.5)b	3.95 (0.04)a	1.8 (0.3)a
Oe + Oa	2.80 (0.05)c	77 (17)b	2.58 (0.02)b	102 (15)b	2.77 (0.06)b	42 (11)a	3.50 (0.19)a	5 (2)a
Mineral soil	2.75 (0.05)c	2790 (770)c	2.85 (0.08)c	2220 (1180)c	3.00 (0.08)b	1690 (1240)b	3.47 (0.10)a	530 (470)a

† Standard error in parentheses, $n = 6$. Common letters among means within rows denote no significant difference at $p \leq 0.05$.

Table 3. Mean cation exchange capacity and acidity pools. Exchangeable acidity includes Al acidity, and titratable acidity includes exchangeable acidity.

Parameter	Plot							
	Control A		Control B		Burn A		Burn B	
	mmol c/kg	kmol c/ha	mmol c/kg	kmol c/ha	mmol c/kg	kmol c/ha	mmol c/kg	kmol c/ha
	CEC							
Oe + Oa	1210 (80)d†	18 (4)d	1120 (60)c	15 (3)c	950 (60)b	8 (2)b	670 (40)a	3 (0.5)a
Mineral soil	310 (20)b	484 (30)b	310 (30)b	479 (39)b	270 (20)a	419 (37)a	210 (20)a	332 (34)a
	Aluminum acidity							
Oe + Oa	31 (5)b	0.4 (0.05)b	64 (14)b	0.8 (0.15)b	33 (3)b	0.3 (0.05)a	5 (2)a	0.04 (0.02)a
Mineral soil	48 (2)b	76 (3)b	58 (4)b	91 (6)b	39 (3)a	61 (5)a	20 (4)a	32 (6)a
	Exchangeable acidity							
Oe + Oa	90 (4)b	1.3 (0.3)b	128 (10)b	1.6 (0.15)b	66 (4)a	0.5 (0.1)a	14 (4)a	0.1 (0.05)a
Mineral soil	64 (4)c	101 (6)c	69 (3)c	109 (5)c	51 (4)b	80 (6)b	26 (5)a	40 (7)a
	Titratable acidity							
Oi	900 (10)d	13 (2)b	760 (30)c	10 (1.5)c	670 (20)b	6 (1)b	580 (10)a	3 (0.5)a
Oe + Oa	1160 (70)c	18 (4)c	1000 (30)c	13 (3)c	770 (50)b	6 (1)b	490 (70)a	2 (0.5)a
Mineral soil	290 (20)a	361 (35)a	300 (20)a	463 (27)a	300 (30)a	468 (42)a	230 (20)a	366 (36)a
Sum		492 (40)b		486 (22)b		480 (44)b		371 (36)a

† Standard error in parentheses, $n = 6$. Common letters among means within rows (and units) denote no significant difference at $p \leq 0.05$.

Table 4. Simple correlation coefficients (r) among variables within samples across all plots (n = 24). All coefficients are significant at p <0.05.

| | Variable | | | | | | | | | |
| Variable | pH CaCl₂ | | | Exchangeable acidity | | Aluminum acidity | | Titratable acidity | | |
	Oi	Oe + Oa	0-10 cm	Oe + Oa	0-10 cm	Oe + Oa	0-10 cm	Oi	Oe + Oa	0-10 cm
pH water	0.90	0.88	0.72	−0.83†	−0.78	−0.60	−0.72	−0.84	−0.79‡	−0.57
pH CaCl₂				−0.81§	−0.84	−0.62	−0.77	−0.85	−0.75¶	−0.41
Exchangeable acidity						0.85	0.97		0.77	0.65
Aluminum acidity									0.40	0.59

† r = −0.96 with log₁₀ (exchangeable acidity).
‡ r = −0.86 with log₁₀ (titratable acidity).

§ r = −0.91 with log₁₀ (exchangeable acidity).
¶ r = −0.82 with log₁₀ (titratable acidity).

mineral soil, a decrease of about 250 kmol H⁺ ha⁻¹ would accompany a 0.5 unit increase in pH.

This between-sample and between-plot approach has two limitations. Changes in acidity kg⁻¹ of horizon

Fig. 1. Soil pH as a function of titratable acidity. See Table 4 for correlation coefficients.

material are confounded with changes in horizon weight. A reduction in total acidity could result from a reduction in weight (with little effect on pH) or a reduction in acidity kg⁻¹ (with a significant effect on pH). More critically, all acids that dissociate below pH 8.2 are included in comparisons among treatments, though only a fraction actually dissociate under ambient conditions.

A second approach examines the patterns of pH and acid pools within samples (Fig. 2) through short-term titration in the laboratory. In this case, changes in pH can be considered in terms of acid neutralizing capacity at any pH rather than solely at pH 8.2. Titration of samples from the more intensely burned plot showed that Oi and Oe + Oa samples required about 100 to 250 μmol H⁺ g⁻¹ to decrease pH to the level of the unburned plots. Multiplying this buffer capacity kg⁻¹ by the biomass of the horizons yields a total buffer capacity (relative to the pH of the controls) for the forest floor of only about 0.5 kmol H⁺ ha⁻¹. The fire consumed a large amount of acidity, but did not convey much residual buffering capacity (= acid neutralizing capacity). Titrations of mineral soil samples from the burned plots revealed that only about 20 μmol H⁺ g⁻¹ was required to reach the pH of the unburned plots, but the large mass of the 0 to 10 cm soil converts to a total buffer capacity of about 25 kmol H⁺ ha⁻¹.

The titration approach also reveals a weakness of using a high-pH endpoint (such as 8.2) to examine changes in acidity. The difference in acid neutralizing capacity between the curves at a given pH increased with pH, indicating the burned plot contained fewer very weak acids (i.e., pK's >5, than the unburned plots. Therefore, the magnitude of the difference in acidity among plots depends upon the pH of reference. Much of the effect of burning on titratable acidity to pH 8.2 was on acids that do not dissociate in the pH region of these extremely acid soils.

These points are illustrated in Table 5. In the Oi horizon, the change in pH of 0.3 units in the more intensely burned plot was accompanied by a decrease of 9 kmol H⁺ of total acidity. Not all titration curves extended to pH 8.2, but at pH 7 the titration curves combined with horizon weights indicated that the Oi from the burned plot would require only 1.1 kmol H⁺ ha⁻¹ to lower its pH to the level of the unburned plots. Thus, the bulk of the reduction in total acidity resulted from combustion of undissociated, very weak acids with little effect on ambient pH. This conclusion is reinforced by comparing the differences between titration curves at pH 7 and pH 4. The quantity of acid
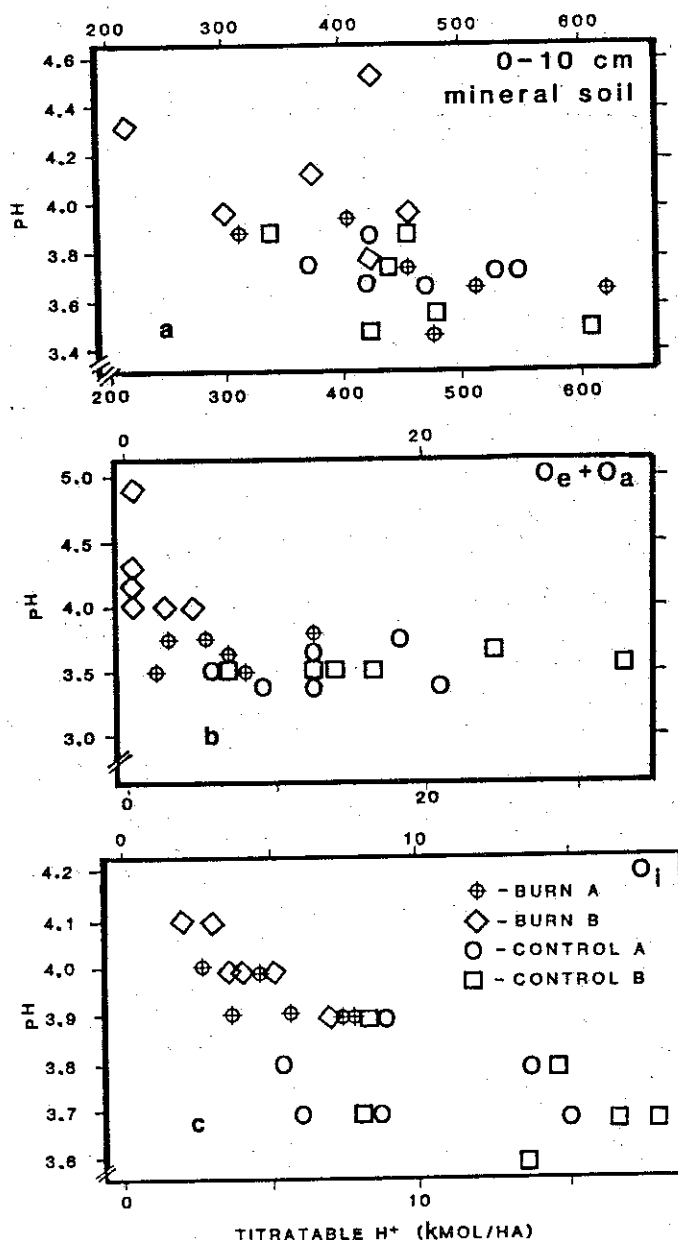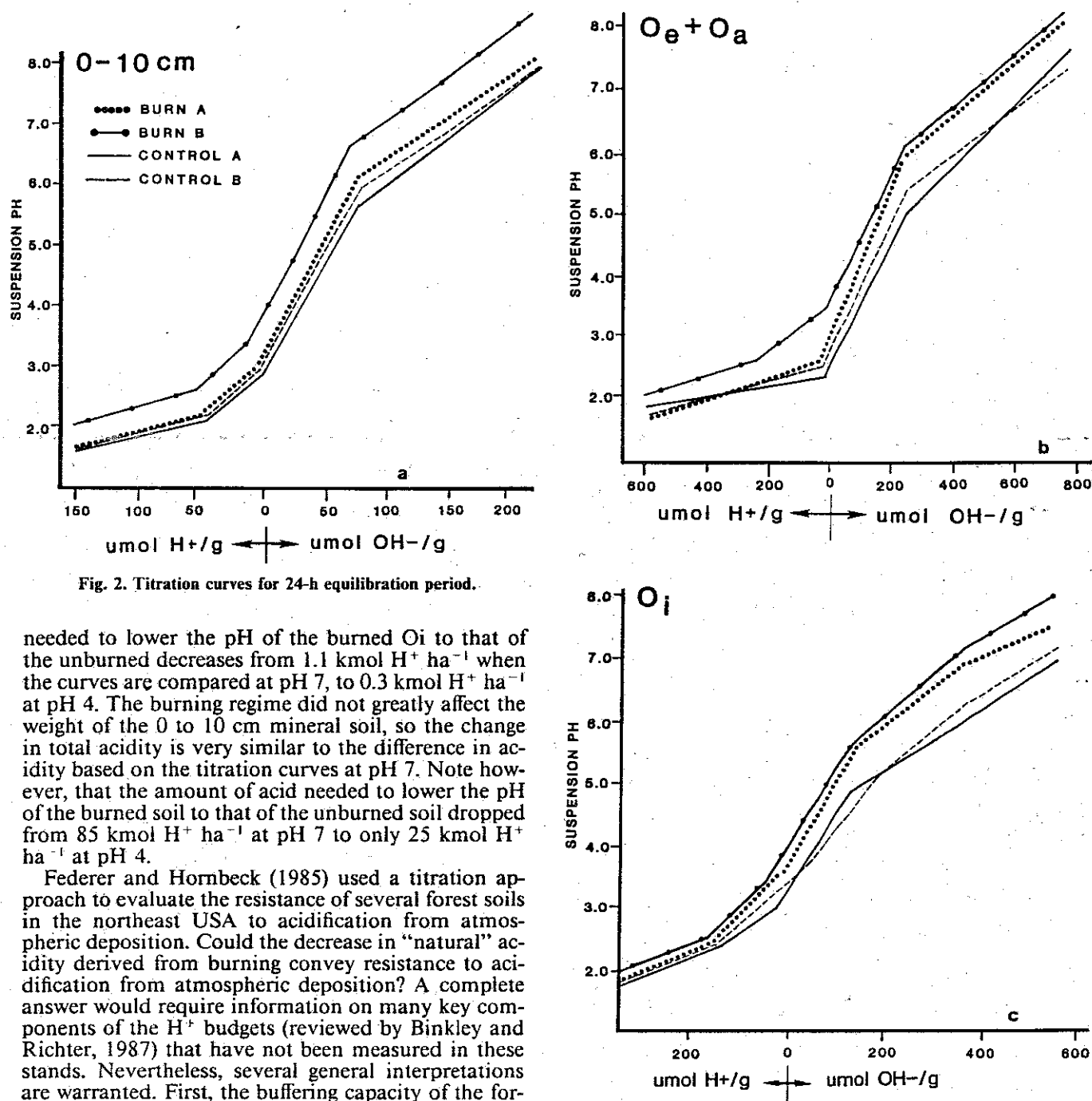
Fig. 2. Titration curves for 24-h equilibration period.

needed to lower the pH of the burned Oi to that of the unburned decreases from 1.1 kmol H^+ ha^{-1} when the curves are compared at pH 7, to 0.3 kmol H^+ ha^{-1} at pH 4. The burning regime did not greatly affect the weight of the 0 to 10 cm mineral soil, so the change in total acidity is very similar to the difference in acidity based on the titration curves at pH 7. Note however, that the amount of acid needed to lower the pH of the burned soil to that of the unburned soil dropped from 85 kmol H^+ ha^{-1} at pH 7 to only 25 kmol H^+ ha^{-1} at pH 4.

Federer and Hornbeck (1985) used a titration approach to evaluate the resistance of several forest soils in the northeast USA to acidification from atmospheric deposition. Could the decrease in "natural" acidity derived from burning convey resistance to acidification from atmospheric deposition? A complete answer would require information on many key components of the H^+ budgets (reviewed by Binkley and Richter, 1987) that have not been measured in these stands. Nevertheless, several general interpretations are warranted. First, the buffering capacity of the forest floor was slight, and fairly minor additions of acid could return the pH to pre-burn levels. Indeed, the burned plots would be less resistant to acidification beyond the pH of the unburned plots due to decreased forest floor biomass. Next, the 25 kmol H^+ ha^{-1} buffer capacity of the more intensely burned plot would appear to provide substantial buffer capacity. Current precipitation in this region averages about 120 cm yr^{-1} with a pH of 4.4 (Gilliam, 1984), representing an input of 0.5 kmol H^+ ha^{-1} annually. The reduction in soil acidity in the more intensely burned plot appears large relative to precipitation inputs, but this interpretation is clouded by failure of the less intensely burned plot to show greater buffering capacity (or lower total ac-

Table 5. Differences in pH and acidity between unburned plots and the more-intensely burned plot.

Horizon	Difference in		H^+ required to make titration curve for burned soil coincide with curve for control soil	
	pH	Total acidity	pH 7	pH 4
			kmol H^+ ha^{-1}	
Oi	0.3†	9	1.1	0.3
Oe + Oa	0.9	14	0.6	0.3
0–10 cm mineral soil	0.4	95	85	25

† Saturated paste pH using distilled deionized water.

idity) than found for the unburned plots. The difference in intensity of the most recent fire accounts for some of the difference, but other factors may also differ between the plots. In addition, high variability among samples within sites provides wide confidence intervals around plot means, making the estimate of the difference between means fairly imprecise even where means differed significantly. Nonetheless, these data are consistent with the hypothesis that burning may convey resistance to soil acidification from atmospheric deposition or other sources by reducing pools of H^+ in forest soils.

The effects of fire in the current study on soil pH was similar to the results of other studies (e.g., Wells et al., 1979; McKee et al., 1982), but data for comparison with changes in other acidity components are lacking. Measurements of acid pools and H^+ fluxes have been common in agricultural research, but few studies of forest ecosystems have gone beyond simple measurements of pH. However, agricultural methods appropriate for estimating acidity and lime potential in mildly acidic conditions may be less informative in the very acid region common for forest soils. A full evaluation of the effects of fire on ecosystem acidity will await studies that quantify all major portions of the H^+ budgets, especially across a range of site types.

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The Influence of Pretreatment Forest Soil Variability on Interpretation of Posttreatment Results[1]

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ABSTRACT

Analysis of covariance procedures were used to evaluate differences in forest soil chemical properties among four site preparation techniques. Comparisons were made between analyses of variance adjusted with pretreatment soil chemical data used as covariates and unadjusted analysis of variance results. These comparisons indicated that failure to adjust for pretreatment spatial variation in soil chemical properties would lead to misinterpretation of the study results. This misinterpretation involved different rankings (for unadjusted vs. adjusted) of the site preparation treatment effects on soil N, P, K, Ca, and Mg concentrations.

Additional Index Words: soil spatial variability, analysis of covariance, site preparation, forest soil chemical properties.

A PRIMARY CONSIDERATION IN PLOT STUDIES is the minimization of error associated with inherent variation within study sites. Cochran and Cox (1957), note that "inherent variability in the experimental material to which treatments are applied" is one of the main sources of experimental error.

The importance of this problem in soil studies is well recognized (Forester, 1937; Mader, 1963; Beckett and Webster, 1971). The problem may be especially acute in forest soils which are generally more heterogeneous than other soils (Pritchett, 1979). The realization that spatial variation in soil properties is usually not random but stratified, has resulted in recent interest in geostatistical techniques such as kriging (Russo, 1984; Grey and Payne, 1985).

Failure to consider soil spatial variability in the design of plot experiments can lead to problems which must be later amended (Pehl 1984). However, even in instances where careful attention is devoted to soil-site characteristics in relation to plot installation, inherent variation can cause treatment effects to be obscured or misinterpreted. Therefore, this study focuses